

SUSTAINABLE ENERGY FROM WASTE BY GASIFICATION AND PLASMA CRACKING, FEATURING SAFE AND INERT RENDERING OF RESIDUES. RECENT EXPERIENCES FOR RECLAIMING ENERGY AND FERROCHROME FROM THE TANNERY INDUSTRY

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Abstract Due to the toxicity of hexavalent chromium (CrVI) there is a growing environmental concern on modern tanning processes. Despite this, chrome tanned leather still accounts for more than 90% of the global leather production. So far no adequate solution to the waste problem has been established in the market. This paper deals with an eco-efficient process that features energy and materials recovery, combined with safe handling and inert rendering of tannery sludge with hardly any adverse environmental impact. The core technology, designated PyroArc®, employs *gasification-melting-vitrification* linked to a *high-temperature-plasma-augmented decomposition chamber* that ensures complete dissociation of the gas. The immediate advantages are: 1) the chromium contained by the sludge is retrieved as molten non-toxic ferrochrome that can be valorised as raw material to the metallurgic industry, 2) the produced gas is cracked into a harmless fuel gas that is used to feed a gas engine, and 3) a complete volume reduction is obtained – with almost no residues for further landfill disposal.

Keywords Tannery waste, gasification, plasma, ferrochrome, fuel gas, energy.

PROBLEM DESCRIPTION

Chromium is used to stabilise the protein collagen from which hides and skins are made [7]. Due to the toxicity of CrVI there is a growing environmental concern on modern tanning processes. During normal conditions, only a harmless CrIII occurs which is explained to present no more risk than common salt. There are, however, some severe toxicological issues with CrVI – especially when it comes to the treatment and disposal of tannery waste – that call for new solutions. In a recent overview article on the upper leather

development Avery [7] explains the role of the automotive upholstery sector in placing a pressure on the leather industry to produce leather without the use of chromium and minerals, - or at least to come up with a product that can be labelled ‘environmentally acceptable’. The truth is, Avery adds, that a commercially acceptable shoe upper leather with a mineral-free tannage, that compares favourably with the broad performance available from a similar one based on a sound chrome tannage, has not yet been produced. Therefore, as long as the future tanning process seemingly will continue to use chromium, it remains a challenge to solve the tannery waste problem in an eco-toxicologically acceptable way.

NEW TECHNOLOGY APPROACH

A proprietary technology designated PyroArc®, protected by intellectual law, has been applied to tannery waste in a most promising manner. The process has been in commercial operation at a tannery on the West Coast of Norway since mid 2001. The process employs *gasification-and-plasma-cracking*. In contrast to most conventional waste processing technologies the PyroArc process is probably the only one to offer the capability of turning the tannery waste problem to a valorising source that may add values to the plant owner in terms of excessive energy and ferrochrome, a harmless alloy that is widely used by the metallurgical industry. The process leaves no ashes but a non-leaching slag that is useful for civil engineering works, and, hence, no residues for landfill disposal (refer Figure 1).

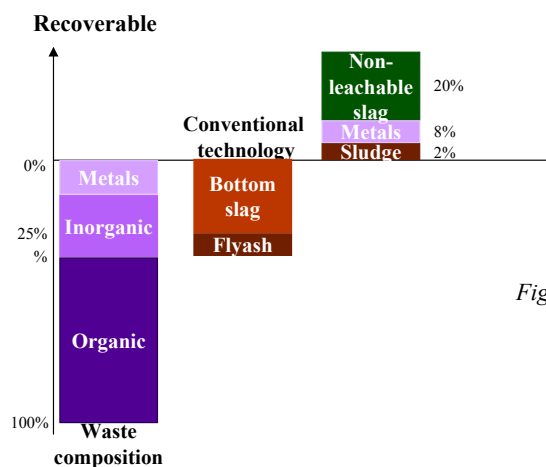


Figure 1: Typical mass fractions of waste (left column) compared to residues from conventional technology with a 70-75% reduction (mid column), and a 100% reduction offered by the PyroArc (right column).

PROCESS AND WORKING PRINCIPLE

Technology description

A concept image of the process is shown on Figure 2. It comprises a *drier-briquetting-feed system (A)*, a *shaft-furnace-gasification reactor (B)*, a *plasma-augmented-high-temperature-mixing-destruction chamber (C)*, a *steam boiler (D)* and a *dust collection-gas-cleaning system (E)* for the capturing of volatile metals and alkaline salts. Further, a consecutive downstream *energy recovery train (F)* is included in the process characterised by combined heat and power (CHP).

The process involves three consecutive conversions:

1. gasification sustained by a counter-current partial oxidation combined with vitrification and melting
2. a complete dissociation of the produced pyrolysis gas combined with *prevention of recombination of the gas* obtained by partial oxidation by secondary air
3. energy recovery by steam generation and CHP involving an a gas engine operating on the produced fuel gas.

Based on a high-temperature plasma jet the process is capable of decomposing the organic materials into basic gas molecules. Typical of the process are the large temperature span and the multiple processes that take place simultaneously - almost within the same enclosure, and also the high efficiency -both electric and thermal. In principle, literally any solid material - except for nuclear waste - can be safely handled. Since the system leaves no bottom ash, nor fly ash, the handling of effluent streams is rather trivial and also environmentally sound.

Tannery waste pre-treatment

The tannery waste consists of organic substances that are removed from the hides and the skins comprising tissue and fat mixed with chemicals required by the tanning process (especially chromium and minerals). The sludge is around 90% water that is osmotically bound and cannot easily be removed by mechanical separation. Therefore a steam-coil drier, Multicoil MCL 2/5-36, operating at 7 – 8 bar steam pressure, is used for the dewatering. Per day some 9 m³ of sludge is dried to a moisture content of only 2%.

Figure 2: Concept image of the PyroArc applied to tannery waste comprising a feed system complete with a steam dryer and briquetting machine (A), a shaft-furnace-gasifier (B), a plasma-augmented-high-temperature-mixing-destruction reactor (C) followed by a steam generator (D) and a gas cleaning unit (E) attached to a gas engine-generator and exhaust boiler (F).

Because dust avoidance in the gasifier is important a water-based organic binding agent is mixed with the dried material adjacent to the briquetting machine so that the mechanical and thermal properties of the briquettes are kept at a pre-set level. The rationale is that a homogeneous distribution of the moisture is required due to the fact that too much humidity would result in a disintegration of the briquettes when charged to the gasifier.

Core technology

The core of the PyroArc process is the *plasma-augmented-decomposition reactor* that is quite essential for achieving a complete dissociation of the pyrolysis gas. The pyrolysis gas enters the plasma zone and expands into an equalising zone and is fully cracked during a total residence time of only 0.3 - 0.6 s. During this conversion process the heating value of the produced fuel gas remains unchanged. The short residence time is motivated by the very high reaction rates in the plasma zone.

The foremost important features are the complete mixing and the instant initiation of the decomposition reactions. Due to the extreme temperatures of the plasma jet combined with the reduction conditions in the reactor no halogens, Cl_2 and Br_2 will be formed. This prevents recombination of halogenated hydrocarbons.

Shaft Gasifier

In order to reach the high reaction rates in the decomposition reactor a well-premixed producer gas is required. This explains the importance of the gasifier when treating solid waste materials. In this concept a blast furnace shaft gasifier is being used - a type that is well known from the steel works. The shaft is an up-draft gasifier that combines easy and rugged design with low thermal losses and long lining life. The solid waste material is charged into the gasifier through a lock hopper system, and the gasifier is fully sealed so that no components can leave the unit without having either been gasified or completely molten.

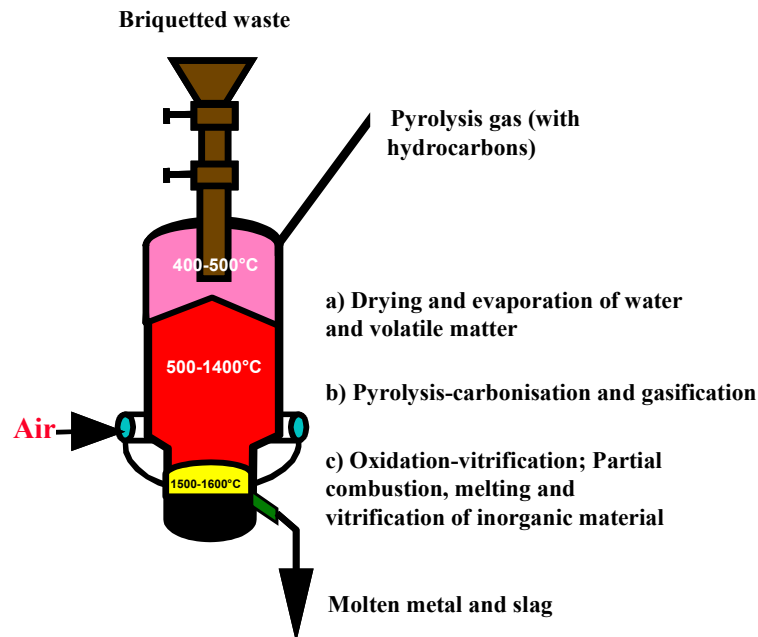


Figure 3: Illustration of the shaft reactor with indication of the characteristic zones

As shown in Figure 3 the shaft reactor can be characterised by three distinct zones:

1. drying and evaporation
2. pyrolysis and carbonisation
3. partial oxidation and vitrification

The internal heat generation is controlled by preheated blast air introduced to the *oxidation-vitrification* zone c). Here the char that descends from the carbonisation zone, is mainly reduced to carbon monoxide that results from under-stoichiometric reactions with preheated air. Owing to exothermic reactions the temperature reaches 1450-1550°C. At this level all inorganic materials are prone to melt, and thus, leaving a homogeneous slag and metals.

The behaviour of metals in the lower zone is slightly different; Metals from the waste (mostly chromium) are collected as molten ferrochrome from the shaft.

In the middle zone (*pyrolysis-carbonisation*) the solid material is being carbonised at a temperature of around 1000°C. The carbon-fix content that is associated with solid organic materials of the tannery waste is rather low – only 5 – 8%, therefore some coke or impregnated wood (biomass) are added so that the actual carbon-fix content reaches around 15% - characterized as a low-grade char. The remaining part will be inorganic substances. Despite such low carbon-fix content the energy from this partial oxidation will still be sufficient to reach temperatures that are required to melt the inorganic components.

All materials with some substantial vapour pressure, such as water and hydrocarbons, evaporate in the upper zone (a) (*drying-evaporation*). A short duct diverts the pyrolysis gas from the top of the gasifier to the decomposition reactor at a temperature of 400-500 °C. At this stage the gas may contain some complex molecules - including halogenated and chlorinated hydrocarbons and other carcinogenic organic gases which makes the pyrolysis gas dangerous!

Plasma generator

Owing to the high-energetic plasma jet that reaches temperature of 3000-5000 °C, the pyrolysis gas is efficiently cracked to a harmless fuel gas that consists of only basic molecules. This implies that the problem with tar that is associated with biogasification, is eliminated at the outset. And, instead of removing the complex HC molecules, some additional heating value will be returned to the fuel gas.

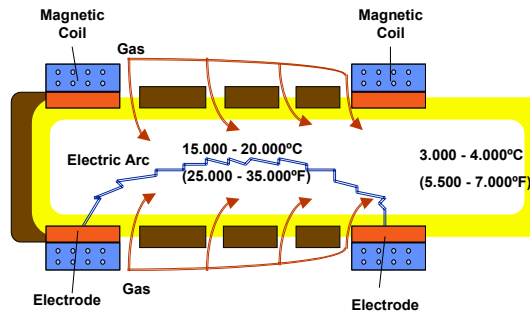


Figure 4: Image of the arc plasma showing in principle how the high temperature plasma is being generated.

An electric arc-plasma generator provides the plasma (Figure 4). The plasma generator is water cooled and purged with compressed air. The enthalpy of the plasma is typically 2 – 2.5 MJ/m³. The electric power required by the plasma generator corresponds to 3-8% of the energy charged to the process by the tannery waste. The main purpose of the plasma is to:

- Provide a zone of high energy density
- Excite strong dynamic forces in order to ensure instantaneous mixing with a uniform temperature profile of the entire gas volume
- Supply heat in order to control the temperature level of the endothermic decomposition reactions (thermal cracking)

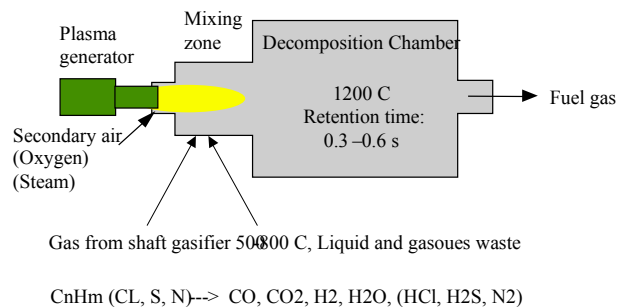


Figure 5: The principle of the plasma generator and how it is connected to the decomposition chamber, and also the introduction of secondary air to provide the cracking. The heat required amounts to 92-97% by partial oxidation and 3-8% electric power [5].

The thermal cracking of the produced fuel gas is characterised by the oxidation rate and controlled by air intrusion to the decomposition reactor as shown on Figure 5. The oxidation rate is based on a continuous recording at reactor outlet of the content of CO and CO₂, and is defined as the fraction of carbon dioxides to the total carbon-oxides as follows from equation (1):

$$R = \text{CO}_2 / [\text{CO}_2 + \text{CO}] \quad (1)$$

The process is controlled according to a simple rule based on keeping the oxidation rate within the range (α and β):

$$\alpha < R < \beta \quad (2)$$

Typical values of α and β are 0.1 and 0.4 respectively. Experience shows that HCN may occur if the oxidation ratio goes below α , and NO_x may be formed if R exceeds β .

Heat Recovery and Gas Cleaning

Following the decomposition reactor, the hot fuel gas is first being quenched by in-line-mixing with re-circulated cleansed fuel gas so that the temperature quickly drops from 1200 °C to 700-800 °C before being introduced to the steam generator. The rationale is to adjust the temperature to a level that is considered suitable for the steam generator.

Some volatile metals like zinc, lead and mercury may evaporise and leave the gasifier as part of the fuel gas and be captured in the down-stream gas cleaning system. It should be noticed that the volumetric flow of the fuel gas from this process amounts only to 30-40% of the corresponding flue gas volume that would result from an incineration process with a similar input of waste. This means that a comparatively larger gas cleaning unit would be required for incineration processes. It should also be noticed that the absence of tar in the fuel gas produced by the PyroArc process, makes the down-stream gas cleaning easier, and will eventually also improve the efficiency of the process. Experience also shows that the emission of mercury depends more on the gas volume than on the total amount of mercury. Hence, a process offering only 30-40% of the gas volume means a substantial reduction in mercury emission [4,5].

PRODUCTS

The outcome of the process is

1. a low calorific fuel gas,
2. leach resistant slag,
3. molten metal

Whereas some 70% of the heating capacity of the waste is retrieved as fuel gas, some 20% will be sensible heat recovered as saturated steam (10 bar pressure) and low temperature heat (below 100 °C).

Fuel Gas

The produced fuel gas is a low calorific gas (LCV) with a heating value of 3.6 - 4 MJ/m_N³. It consists essentially of basic molecules such as hydrogen (12 – 15%), CO (17 – 22%), CO₂, N₂ and water vapour. Recordings of the dioxin level of the fuel gas is efficiently used to interpret the extent of the decomposition of the pyrolysis gas. All prior tests based on materials ranging from household waste to concentrated PCB oils, carried out in a 500 kg/h pilot plant at ScanArc's facilities in Hofors, Sweden, show that the dioxin level was kept well below 0.1 nanograms per cubic meter of fuel gas [4,5]. Eventually, all emissions were kept well below the strictest regulations for waste incineration. Since fuel-borne NO_x is low, the NO_x emission of the plant depends on the gas engine only (or the back-up combustor whenever used).

The fuel gas is associated with some quite important aspects:

- No hexavalent chromium present in the fuel gas (all chromium converted to ferrochrome and recovered in molten phase at the bottom of the shaft)
- Practically no dioxins and no chlorinated and halogenated hydrocarbons present
- No complex HC chains that are prone to form tar at lower temperatures
- Less than 30 ppm NO_x (even for the treatment of nitrates)
- Sulphur appears mainly as metal sulphides (it is desirable, though, to turn the sulphur into sulphates that can be discharged to the sea)
- The capture of volatile metals (i.e. small amounts of mercury, zinc and lead) either as secondary dust or venturi sludge.

Slag

The slag properties generally depend on the waste material – and the way the process is operated. In some cases the fraction of silica in the waste may be

insufficient for ensuring a glassy structure with low leaching values – as is the case for tannery waste. In such cases some suitable slag formers (e.g silica sand) are charged to the gasifier in order to influence the slag properties. This may affect the acidity of the slag and ensure that the slag becomes glassy. Experience shows that if the slag turns alkaline, the leaching resistance will suffer, and vice-versa. A Dutch laboratory has validated the leaching resistance of the slag in accordance with the Dutch U1 standard. The following table lists the leaching values of some important elements. The test was based on slag reclaimed from the PyroArc process, and compared to normal bottom ash from municipal solid waste (MSW). The values clearly show that the properties of slag from the PyroArc process are well below the limits given by the U1 standard. This means that the slag can be used for house building purposes.

Table 1

Leaching resistance (mg/kg) of slag:

Technology	PyroArc MSW	Bottom ash MSW	Dutch U1 limits
<i>Elements</i>	<i>mg/kg</i>	<i>mg/kg</i>	<i>mg/kg</i>
As	<0.01	0.14	0.3
Ba	0.017	190	4
Cd	<0.0007	2.4	0.1
Co	0.0014	1.9	0.2
Cr	0.75	1.4	1
Cu	0.071	375	0.35
Hg	N/A	N/A	0.005
Ni	0.19	12	0.35
Pb	0.01	49	0.8
V	<0.1	0.75	0.7
Zn	0.08	1120	1.4

According to Dutch U1-standard (CEN TC 292)

Metals

The chromium content of the tannery waste is recovered as molten ferrochrome that has a commercial interest in the metallurgic industry. Eventually, since iron (usually) is not a constituent of the tannery sludge some

iron must be supplied to the shaft in order to favour these metallurgic bonds. Owing to the ability of the PyroArc process to transform the chromium into ferrochrome, no hexavalent chromium will be present in the shaft, and hence, the CrVI problem is resolved.

Generally, all metals with affinity to oxygen lower than iron can be recovered as molten metal, whereas metals with a higher affinity (like Al, Ti, Mg) are prone to oxidise and dissolve in the slag. To the extent that some volatile metals (e.g. Zn, Pb, Hg) are present in the feed these metals may be reclaimed as secondary dust.

EXPERIENCES

In 2001 the Norwegian based company, Borge Garveri AS, took delivery of the first bona fide PyroArc tannery waste treatment plant. Over the first ¾ year since commission was started, the plant has cumulated more than 4000 operating hours, and the process has successfully demonstrated all of its technical and environmental capabilities. Some improvements have been made over this period, however, mostly minor adjustments.

Operation

The process is running stable five days per week. According to regulations that apply for processes treating molten metals the plant has to be attended by two shift operators. In order to secure a proper operation an extensive training of the operators was given high priority. In addition to theoretical education this included an on-job training programme jointly with supplier's personnel.

Energy and performance characteristics

From a wet tannery waste flow of 560 kg/h (reckoned to 15% humidity) having a heating value of 3.93 kWh/kg, 1320 m_N³/h of fuel gas is formed with a calorific value corresponding to 1 kWh/ m_N³ and a sensible heat of around 800 kW. This gas is further used to form 415 kW electric power and some 1000 kW of steam (at 8 bar pressure) for the drying process.

Steam generation

In the present configuration the process is generating too small amounts of steam. The explanation is that the moisture content of the tannery sludge in some periods exceeds the design level of the process. Instead of 80% water content,

the current water fraction amounts to over 90%. In order to remove more water, more steam will be needed. This would require increased energy input to the plant. Otherwise the performance would suffer. Therefore the plant is now receiving impregnated wood (biomass) which also is replacing the used of coke. This will make the process self-sustained on steam and electricity. All low temperature heat, available at 70-90 °C, is fully utilised by the tannery process.

Engine

The combined heat and power system (CHP) is based on a Jenbacher 320 gas engine rated at 600 kW. At normal operating conditions some imbalance may occur between the electric power output and the steam generation. When operating the engine a full load the steam generation may suffer, and hence the drying process will go slow. The introduction of additional biomass (as mentioned in the above section) will improve this situation.

Wear and tear

The normal lining life of the refractory walls will usually be some 4 – 5 years at continuous operation. So far there is no indication of wear and tear in the gasifier. However, some wear on the refractory of the decomposition chamber. This is mainly explained by low cycle fatigue owing to the rather larger number of hot and cold cycles. In order to reduce the number of starts and stops, an extension from five days to a continuous seven days a week operation would be desirable. Since this would require larger amounts of waste than the tannery itself can provide, the reception of industrial solid waste (and some MSW) would be necessary.

Plasma

The plasma generator requires a power input that corresponds to 300-400 A at 1100V. The plasma has caused no problem whatsoever.

Sulphur

There has been some initial problems with sulphur emissions which has now been adjusted to below the limits given by the regulation. However, an increased margin would be preferable in future applications. Therefore, ways of further reducing the sulphur emission are being pursued.

Carbon monoxide (CO)

Being a thermo-chemical process characterised by partial combustion at understoichiometric conditions, gasification, in contrast to incineration processes, is aimed at generating so much heat that pyrolysis may keep going, and, at the same time leaving so much heating value as practical for the produced gas. Since carbon monoxide represents a substantial heating value (some 10200 kJ/kg) CO is a desired product together with hydrogen. Obviously, it makes no sense to compare the fuel gas and the flue gas from such processes. However, when burning the fuel gas produced from the tannery waste in a bypass combustor the corresponding CO content of the flue gas will be no more than 50 mg/m_N³ in accordance with the regulations

It is well known that gas engines are prone to emit CO when operated on LCV gases. The reason is that a LCV gas due to its deficient energy cannot provide the high temperature needed for a complete reduction of CO to CO₂ within the short time frame available for the combustion in a reciprocating engine. Thus, a CO-emission limit of 3000 mg/m_N³ was decided in regards of the gas engine only. It should be noticed that even for pure methane (natural gas) the regulation allows for 500 mg/m_N³ CO for modern gas engines. This is ten times higher than the limit set for waste incineration. Although engine manufacturers suggest some initiatives for future CO emission reduction, this can only be achieved on a long-term perspective (and to a limited extent).

Slag

So far the leach-resistant slag is used only for local landfill purposes with no precaution.

Emissions

The emission figures of the plant are shown in Table 2. The cited limits were all approved by the Norwegian Pollution Authority Control, SFT. These limits are used as reference for the process. As can be seen all components (except for sulphur) are kept below the specified limits.

Table 2**Emission figures of the tannery process**

<i>Component</i>	<i>Comment/ amount of air</i>	<i>Limitations</i>			<i>Recorded</i>	
		<i>Limit</i>	<i>Unit</i>	<i>Mean time</i>	<i>Mean</i>	<i>Highest</i>
Cd	Cd and Ti	0.05	mg/m _N ³		0.000037	0.000043
CO	30 min. decided by gas engine	3000	mg/m _N ³	h	3000 50	60
Dioxin		0.1	ng/m _N ³		0.05	0.05
HCl	30 min. inorganic chlorine	60	mg/m _N ³	h	1.3	1.5
HCl	inorganic chlorine	10	mg/m _N ³	d	<0.2	<0.2
HF	30 min. inorganic fluor	4	mg/m _N ³	h	-	-
HF	inorganic fluor	1	mg/m _N ³	d	0.06	0.2
Hg		0.05	mg/m _N ³	d	0.001	0.01
Instov	30 min.	30	mg/m _N ³	h	1.7	1.9
Instov		10	mg/m _N ³	d	-	-
Metals	div. metals	0.5	mg/m _N ³		0.0075	0.0084
NOx	as NO ₂	400	mg/m _N ³	h	4	
NOx		200	mg/m _N ³	d	80	
SO₂	30 min.	200	mg/m _N ³	h	152	350
SO₂		50	mg/m _N ³	d	100	-
TOC	30 min.	20	mg/m _N ³	h	-	
TOC (iii)	Basically CH ₄ + C ₆ H ₆	10	mg/m _N ³	d	<0.020	

FURTHER APPLICATIONS

The development of the PyroArc process has been strongly supported by extensive testing in a technology demonstrator at the premises of ScanArc, Sweden. The process has proved to be robust and suitable for converting almost any solid waste with efficient recovery of energy and materials, and, thus, being capable of receiving literally any waste material except for nuclear. The process will be offered in modules ranging from 10 to 50 thousand tonnes per year – which is seen as a suitable range for future waste-to-energy solutions to local modern societies, particularly in remote regions and touristic islands. A significant market is further identified for local treatment of industrial and

hazardous waste combined with multi-recovery of metals and energy [6]. An example to mention is the treatment of electronic waste which represents a substantial valorising potential because of precious metals (Cu, Au, Pt).

The Norwegian company EnviroArc Technologies AS, is responsible for the sales and marketing of the PyroArc technology.

CONCLUSIONS

Despite the toxicity of CrVI that is associated with modern tanning, still some 90% of the global leather production is chrome-tanned leather – and still chrome tanning is likely to continue for reasons of superb leather quality. However, a pressure is placed on the tanning manufacturers to come up with solutions that can be labelled '*environmentally acceptable*'. Therefore, there is an obvious need for a new technology that is capable of handling the tannery waste problem adequately. It is assumed that only processes that recover metals and minerals with no adverse emissions or effluent streams, may be successful.

One candidate technology – and probably the only one - is the patented PyroArc® process that has recently successfully demonstrated its performance for more than 4000 operating hours at a modern tannery. The process employs *gasification* with *melting-and-vitrification* and a *plasma-augmented decomposition reactor*. This combination is deemed instrumental for achieving the desired 'environmentally acceptable' label. In principle, the PyroArc process can safely handle literally any solid waste materials - except for nuclear. The system leaves no bottom ash, nor fly ash, and, hence, there will be hardly any residues for landfill disposal. Therefore the process is conceived as environmentally sound. There will be practically:

- No hexavalent chromium since the chromium of the waste is converted to ferrochrome and slag that are recovered as molten phases at the bottom of the shaft
- No toxic gases
- No complex HC chains to form tar at lower temperatures
- No volatile metals

And, there will be:

- Less than 30 ppm fuel NO_x, and
- Mainly only metal sulphides from the sulphur

The message to the market is that the PyroArc process has approved its ability to omit the CrVI problem by converting the chromium and the minerals used in

modern tanning processes are converted to ferrochrome and non-leaching slag. Independent laboratory tests, compared to the Dutch U1-standard, show that the leaching resistance of the slag is so high that the slag can be used for house building purposed without concern. Furthermore, the PyroArc process is self-sustained in terms of energy, and is well suited for receiving biomass and industrial waste on commercial conditions in addition to the tannery waste, and may, thus, even deliver excessive electricity to the grid.

It is to be hoped that the experience and results gained by the first operating year may pave the road to a wide-stretched and needful tanning market.

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